February 2004 • NREL/SR-540-35334

Subcontractor Report

Fuel and Fuel Additive Registration Testing of Ethanol-Diesel Blend for O_2Diesel, Inc.

E. Robert Fanick
Southwest Research Institute
San Antonio, TX

O_2Diesel, Inc.
Newark, Delaware

National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401-3393

NREL is a U.S. Department of Energy Laboratory
Operated by Midwest Research Institute • Battelle

Contract No. DE-AC36-99-GO10337

February 2004 • NREL/SR-540-35334

Fuel and Fuel Additive Registration Testing of Ethanol-Diesel Blend for O_2Diesel, Inc.

E. Robert Fanick
Southwest Research Institute
San Antonio, TX

O_2Diesel, Inc.
Newark, Delaware

NREL Technical Monitor: R. McCormick

Prepared under Subcontract No. ZCL-3-32068-01

National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401-3393

NREL is a U.S. Department of Energy Laboratory
Operated by Midwest Research Institute • Battelle

Contract No. DE-AC36-99-GO10337

NOTICE

Available electronically at http://www.osti.gov/bridge

Available for a processing fee to U.S. Department of Energy
and its contractors, in paper, from:
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865.576.8401
fax: 865.576.5728
email: reports@adonis.osti.gov

Available for sale to the public, in paper, from:
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800.553.6847
fax: 703.605.6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/ordering.htm

Printed on paper containing at least 50% wastepaper, including 20% postconsumer waste

Foreword

O2Diesel, Inc. (formerly AAE Technologies, Inc.) conducted this project under subcontract number ZCL-3-32068-01 with the National Renewable Energy Laboratory of the United States Department of Energy. The Office of Energy Efficiency and Renewable Energy, Biomass Program sponsored this effort. Southwest Research Institute performed this project for O2Diesel, Inc. as a lower tier subcontractor. Messrs. Jim Peeples and Paul Vind were the technical representatives for O2Diesel, Inc. Work was performed under SwRI Project 08-06553, and the Principal Investigator and Project Leader for SwRI was Mr. E. Robert Fanick, Group Leader in the Department of Engines and Emissions Research. Dr. Joe Pan in the Petroleum Products Department was responsible for the PAH and NPAH analysis. The SwRI Project Manager for this work was Dr. Lawrence R. Smith, Manager of the Light-Duty and Unregulated Emissions Section.

Executive Summary

Testing was performed on a heavy-duty diesel engine in support of the Environmental Protection Agency (EPA) requirements for registration of designated fuels and fuel additives (F/FA) as stipulated by sections 211(b) and 211(e) of the Clean Air Act (CAA). Emission generation, collection, and analysis of the regulated emissions and speciation of vapor-phase and semi-volatile hydrocarbon compounds were performed on a Detroit Diesel Series 60 engine manufactured in 2002 and meeting the 1998 federal heavy-duty emission standards that applied in 2002. The engine was first tested with O_2Diesel™ (diesel fuel with 7.7% ethanol and additives) after 125 hours of engine operation with the fuel. Testing involved one cold-start test and six hot-start tests on each of three different days. Samples were collected and analyzed for regulated emissions including total hydrocarbons (THC), carbon monoxide (CO), oxides of nitrogen (NO_x), and total particulate; for hydrocarbon speciation; and for semi-volatile (vapor- and particulate-phases) polycyclic aromatic hydrocarbons (PAH) and nitrated polycyclic aromatic hydrocarbons (NPAH). The fuel was then changed to the 211b baseline fuel. After approximately five hours of engine operation with the baseline fuel, the above test sequence was repeated.

In general after 125 hours of operation, both fuels gave regulated emissions that were lower than or equal to the corresponding 2002 emission standards when used in the Detroit Diesel engine with the exception of particulate. Particulate, oxides of nitrogen, and carbon monoxide emissions were found to be lower with O_2Diesel™ when compared to the 211b baseline fuel, and the hydrocarbons were higher (See Summary Table). Speciation of C_1 to C_{12} hydrocarbons, C_1 to C_6 alcohols and ethers, aldehydes, ketones, and vapor- and particulate-phase PAH and NPAH compounds revealed that no additional compounds were present in the exhaust when the emissions were compared to the exhaust from 211b baseline fuel. Ethanol and five aldehydes or ketones (formaldehyde, acetaldehyde, acrolein, acetone, and benzaldehyde) were detected at concentrations greater than the 211b baseline fuel, but these results are considered typical of engines operating on fuels containing ethanol. No additional compounds which could be attributed to O_2Diesel™ were found in the exhaust above the detection limits for the analytical procedures, except for an unidentified C_8 compound which was detected in only two of the hot-start tests with the O_2Diesel™.

Summary Table of Composite Regulated Emissions

Test	Emissions Results, g/bhp-hr			
	THC	CO	NO_x	Particulate
2002 Standard	1.3	16	4.0	0.10
O_2Diesel™				
Composite C1-H11	0.27	1.5	3.4	0.13
Composite C2-H21	0.27	1.5	3.6	0.13
Composite C3-H31	0.31	1.6	3.6	0.13
Average of Three Composites	0.28	1.5	3.6	0.13
211b Baseline Fuel				
Composite C1-H11	0.16	1.6	3.8	0.13
Composite C2-H21	0.24	1.6	3.8	0.14
Composite C3-H31	0.21	1.7	3.7	0.15
Average of Three Composites	0.20	1.6	3.8	0.14

Table of Contents

Figures

Tables

I. Introduction

This work was performed for O_2Diesel, Inc. in support of the Environmental Protection Agency (EPA) requirements for registration of designated fuels and fuel additives (F/FA) as stipulated by sections 211(b) and 211(e) of the Clean Air Act (CAA). In general, standard mandatory requirements for F/FA registrations are contained in a three tiered structure. The first two tiers generally apply to most F/FA manufacturers, but there are special provisions for certain types of additives and small businesses. Each manufacturer is required to submit basic registration data for each product being registered. Small businesses with less than $50 million of annual sales are excused from the first two tiers of requirements for F/FA which are considered baseline or non-baseline, and small businesses with less than $10 million annual sales are excused from Tier 2 requirements for "atypical" F/FA. Definitions of baseline, non-baseline, and "atypical" F/FA are discussed in detail below. The other special provisions include experimental F/FA, relabeled products, and those exclusively for off-road use.

Each F/FA is sorted into one of two broad "fuel families:" conventional or alternative. The conventional fuel families are gasoline and diesel, and the alternative fuel families include methanol, ethanol, methane, and propane. Each fuel family is then subdivided into three "F/FA categories:" baseline, non-baseline, and "atypical." The baseline category consists of fuels and associated fuel additives which resemble the respective base fuel for a particular fuel family in terms of elemental composition (no elements other than carbon, hydrogen, oxygen, nitrogen, and sulfur), and which conform with certain quantitative limits for particular constituents. "Atypical" is defined as those which contain metals; or elements other than carbon, hydrogen, nitrogen, sulfur, and oxygen. The non-baseline category is an intermediate category between baseline and atypical. In the diesel fuel family, the distinction between baseline and non-baseline is based primarily on the presence of significant concentrations of oxygen-containing compounds (greater than 1.0% oxygen by weight). O_2Diesel™ does not contain any elements other than carbon, hydrogen, oxygen, nitrogen, and sulfur; and falls into the non-baseline fuel family for diesel because it exceeds the 1.0% wt. oxygen limit. This report includes the emission measurements as part of the requirements for the registration of an additive or fuel as stipulated by sections 211(b) and 211(e) of the CAA.

II. Heavy-Duty Engine Testing

A. Objective

The objective of this program was to provide O_2Diesel, Inc. with the generation, collection, and analysis of combustion emission samples. Emissions generation, collection, and analysis were performed according to the Tier 1 requirements as identified in 40 CFR 79.57. Protocols outlined in 40 CFR 86 Subpart D and in applicable SwRI Standard Operating Procedures (References 1 through 20) were followed.

B. Scope of Work

1. Heavy-Duty Test Protocol

Fuel and fuel additive registration testing for Tier 1 utilizes the EPA transient test protocol. The test plan used for the generation and collection of combustion emission samples is shown in Table 1. Under the transient Federal Test Procedure (FTP), the EPA transient cycle is described by means of percent of maximum torque and percent of rated speed for each one-second interval over a test cycle of 1199 seconds duration. To generate a transient cycle, an engine's full load torque curve is obtained from an engine speed below curb idle speed to maximum no-load engine speed. Data from this "torque curve," or torque map, are used with the specified speed and load percentages to form a transient cycle. A graphic presentation of the speed and torque commands which constitute a transient cycle is given in Figure 1 for illustration purposes. The first five minutes of the cycle is designated as the New York Non-Freeway (NYNF) portion of the test and represents city operation with extensive idle time. The second five minutes is called the Los Angeles Non-Freeway (LANF) portion. This part of the test also represents city operation, but without the excessive idle time. The third five minute section of the test is called the Los Angeles Freeway (LAF) portion. This part is more representative of higher speed conditions indicative of freeway operation. The final five minutes of the EPA transient cycle is a repeat of the NYNF portion. These four parts are combined to give the EPA transient cycle.

In general, a transient test consists of both cold- and hot-start EPA transient cycle operation. The same engine command cycle is used in both cases. For the cold-start, the diesel engine is operated over a "prep" cycle, then allowed to stand overnight in an ambient soak at a temperature between 68 and 86°F. The cold-start transient cycle begins when the engine is cranked for cold start-up. Upon completion of the cold-start transient cycle, the engine is stopped and allowed to stand for 20 minutes. After this hot-soak period, a hot-start EPA transient cycle begins with engine cranking. In order to determine how well the engine followed the transient command cycle, engine performance is compared to engine command, and several statistics are computed. These computed statistics must be within tolerances specified in the Code of Federal Regulations (CFR). In addition to statistical parameters, the cycle work actually produced should be between 5 percent above and 15 percent below the work requested by the command cycle.

Table 1. Test Plan for Heavy-Duty Engine Testing

Step	Description
1	Perform emission instrument calibrations as required. Calibrate torque meter and check signal conditioning systems. Validate Constant Volume Sampler (CVS) gaseous and particulate sampling systems using propane recovery techniques.
2	Install engine in transient-capable test cell and check engine condition. Engine must be new with less than 12 hours of previous operation. Bring engine oil level to "full" using oil specified by the manufacturer.
3	Perform fuel change procedure to O_2Diesel™. Change fuel filters, purge fuel supply, etc. Perform 125 hours of engine operation with the Cummins durability cycle.
4	Repeat Step 1 as necessary. Operate engine at rated speed and full load for approximately 10 minutes, then power validate engine.
5	Conduct transient “full-throttle” torque map from low- to high-idle, and save resulting transient command cycle.
6	Run at least two 20-minute practice EPA transient cycles without engine-off soak between cycles, and adjust dynamometer controls to meet statistical requirements for transient cycle operation.
7	Soak engine overnight. Run a cold-start transient cycle. Soak engine for 20 minutes. Run six hot-start transient cycles with a 20 minute engine soak between each one. During the cold- and the first hot-start cycle, collect samples continuously for regulated emissions, total particulate, speciation of volatile hydrocarbon compounds, aldehydes, ketones, alcohols, ethers, and particulate-phase polycyclic aromatic hydrocarbons (PAH) and nitrated polycyclic aromatic hydrocarbons (NPAH) emissions. During all seven tests, collect samples for vapor-phase PAH and NPAH emissions. Combine samples to get a single weighted sample for each test day (one seventh cold- and six/sevenths hot-start).
8	Repeat Step 7 two additional times on different days.
9	Perform fuel change procedure using 211b baseline fuel. Change fuel filters, purge fuel supply, etc.
10	Repeat Steps 4 through 8.
11	Summarize data and prepare final report.

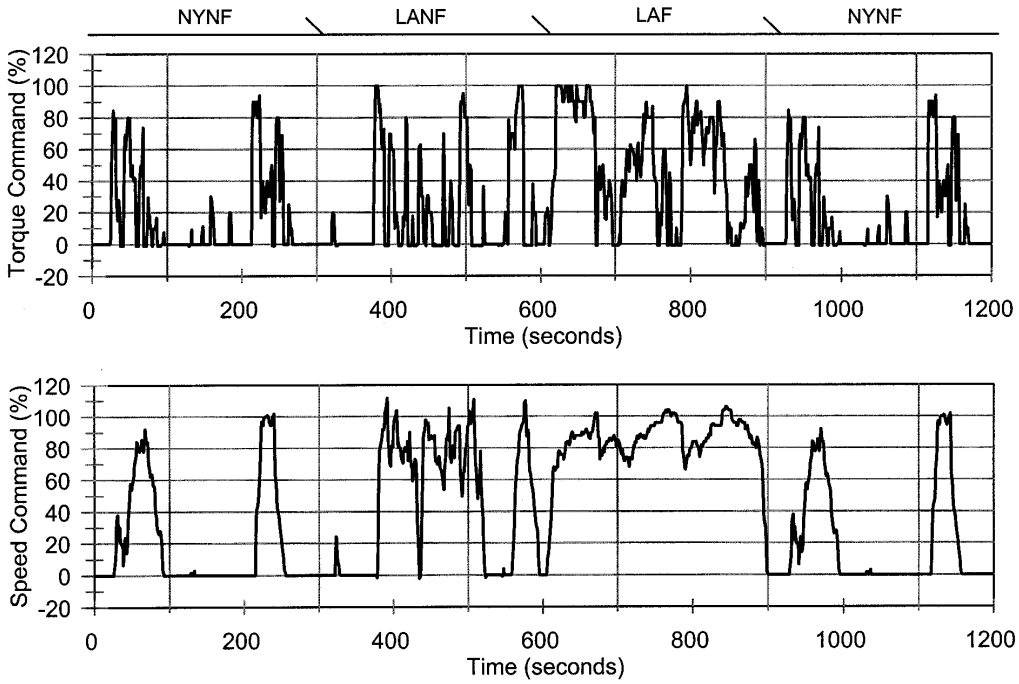

FIGURE 1. GRAPHIC REPRESENTATION OF TORQUE AND SPEED COMMANDS FOR THE TRANSIENT CYCLE FOR HEAVY-DUTY ENGINES

2. Heavy-Duty Engine Selection and Description

For the purpose of testing O_2Diesel™, a 2002 Detroit Diesel (Serial No. 06R0697970) was selected and provided to SwRI by O_2Diesel, Inc. The engine was selected to meet the following criteria:

- Less than 12 hours on the engine chronometer
- Same type, class, and subclass which consumed the most gallons of fuel in the fuel family over the past three years
- Represent the most common fuel metering system and the most common of the most important emission control system devices or characteristics with respect to the emission reduction performance for the model year in which testing began
- One of the five highest selling models from the current model year
- Unaltered from the specification of the original equipment manufacturer and to remain under the control of SwRI throughout the testing.

Table 2 lists the engine specifications and features, and Figure 2 shows the engine mounted on the test stand.

Table 2. Engine Specifications and Features

Engine Parameter	Comment
Engine Type	Diesel, 4-Cycle
Model	6067-MK60 Series 60® - Truck
Serial No.	06R0697970
Configuration	L-6
Displacement	12.7 L (778 CID)
Bore and Stroke	5.12 in. X 6.30 in.
Aspiration	Turbocharged
Rated Power at rpm	400 hp at 2100 rpm
Peak Torque at rpm	1550 lb-ft at 1200 rpm
Idle Speed	600 rpm
Governed Idle Speed	2225 rpm
Combustion System	DI, TC, ECM, CAC (Air to Air)
Engine Family	2DDXH12.7EGL
Certification	2002 Line Haul
Date of Manufacture	7/2002

FIGURE 2. DETROIT DIESEL SERIES 60® MOUNTED ON TEST STAND

3. Engine Mapping and Aging Cycle

After the engine was received from O_2Diesel, Inc., it was operated for 125 hours with the O_2Diesel™ using the Cummins durability cycle. Table 3 presents the durability cycle. The cycle requires about 15 minutes to complete and includes extended operation at peak torque and rated power. At the start of each cycle, the engine idles for 144 seconds before starting high power operation. The durability cycle was conducted on a continuous basis to obtain the designated hours of engine operation.

Table 3. Cummins Durability Cycle for Aging and Engine Deterioration Factor Determination

Cycle Description	Time, sec
Idle	144
Peak Torque	36
Rated Power	360
High Idle	36
Rated Power	144
Transition to Peak Torque	36
Peak Torque	108
High Idle	36
Total	900

Emission testing was performed on the engine at the 125-hour point with the O_2Diesel™. Figure 3 illustrates the engine map used for the O_2Diesel™ tests at 125 hours. Testing consisted of three cold- and eighteen hot-start EPA transient sequences with one cold- and six hot-starts performed on each day. At the completion of the testing, the fuel was changed to the 211b baseline fuel. About five hours of engine operation were then performed. The full emissions characterization sequence with three cold- and eighteen hot-start transient tests was then repeated. Figure 4 illustrates the engine map used for the emissions characterization tests with the 211b baseline fuel.

4. Fuel Blending and Analyses

The 211b baseline fuel (EM-4870-F) was obtained as a single batch from Halterman Products. Sufficient fuel was obtained to perform the initial 125 hours of durability operation and emissions characterization testing with both fuels. This base fuel was used to blend the O_2Diesel™ which initially contained 0.6 percent OCTIMAX™ 4931, but the concentration was later raised to 1.0 percent because of phase separation of the fuel. This situation will be discussed in detail below.

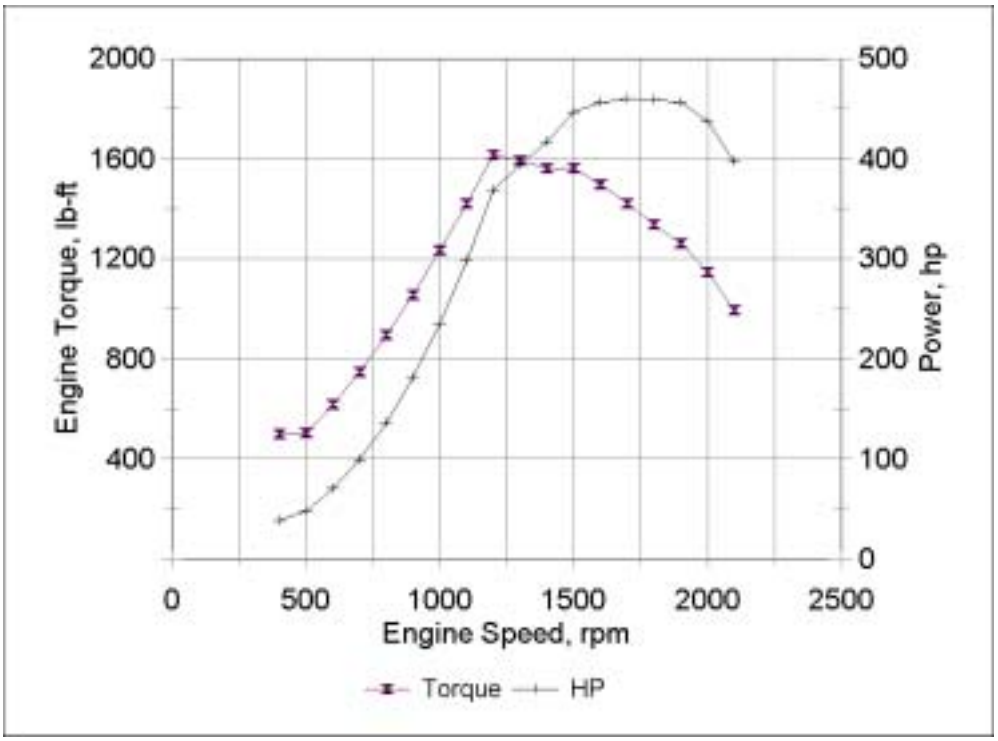

FIGURE 3. SPEED AND TORQUE MAP WITH O_2DIESEL™

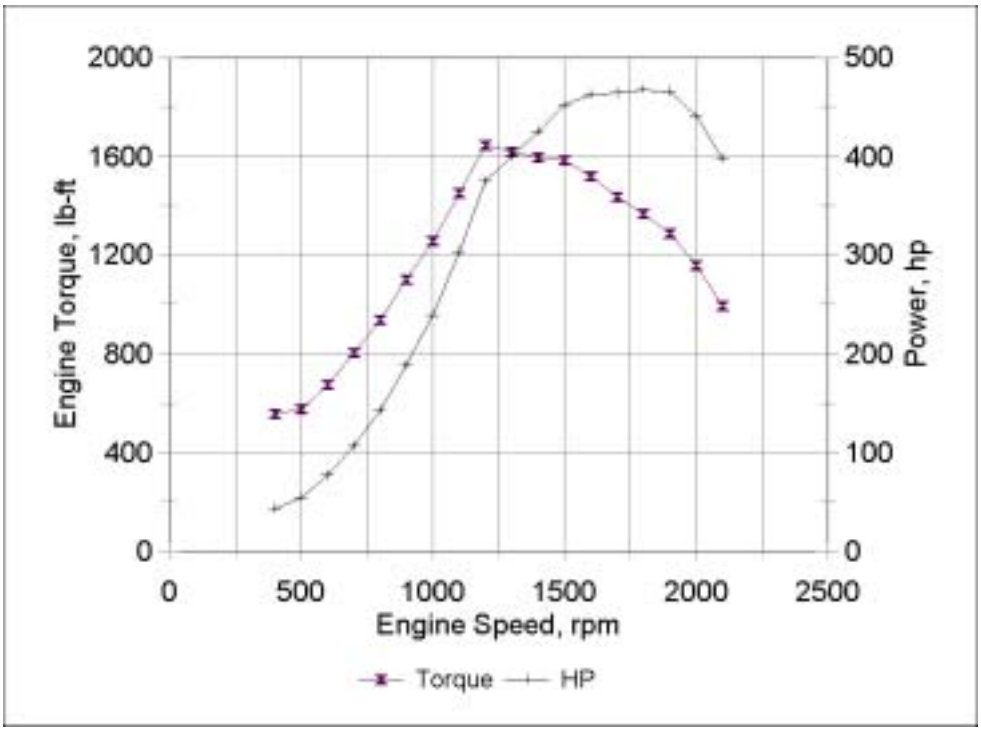

FIGURE 4. ENGINE SPEED AND TORQUE MAP WITH 211b BASELINE FUEL

To obtain the ethanol-based diesel fuel formulation, about 2800 gallons of the 211b baseline fuel were blended according to the amounts listed in Table 4. The fuel formulation was blended by starting with anhydrous ethanol provided by O_2Diesel, Inc. OCTIMAX™ 4931, a proprietary additive technology from O_2Diesel, Inc., was then blended with the ethanol in drums before adding to the main tank. A sample of the ethanol was analyzed by ASTM prior to blending (See Table 5). This mixture was then blended with the 211b baseline fuel by circulating the tank for about two hours. (Note: This procedure was utilized for the purposes of blending the fuel for durability only.) Durability operation was begun with the 0.6 percent concentration of OCTIMAX™ 4931; however, durability was stopped at approximately 30 hours when a problem with the engine developed. This problem lead to an examination of the fuel.

Table 4. Initial Blending Components for Preparing O2Diesel

Blending Component	Volume Percent	Volume, gallons
Denatured ethanol	7.7	233.4
Base Fuel	91.3	2780
OCTIMAX™ 4931	0.6	18.2

Table 5. Ethanol Analysis by Protocol D-4806

Method	Property	Result
D1613	Acidity	0.0066 Mg KOH/g
D4052s	API@60F	47.2
	Specific Gravity@60F	0.7912
	Density@15C	0.8
D4176	Clear &Bright	Clear & Bright
	Particulate	No
	Free Water	No
	Haze	1
D5453	Sulfur Conc.	1.8 ppm
D5501	Ethanol	95.81 wt. %
		96.54 vol. %
	Methanol	<1 wt.%
D5827	Chloride Content	0 ppm
D6304	Water Content	0.852 %
D6423	pHe	7.45
D381	Unwashed Gum	3 mg/100 mL
	Washed Gum	<0.5 mg/100 mL
	Copper Content	<0.05 ppm

Phase separation of the fuel was noted in the main fuel tank. Samples were taken at various depths within the tank (bottom, one foot from the bottom, two feet from the bottom, and at the top of the fuel in the

tank which was about 3 feet from the bottom). These samples were sent for analysis by ASTM D5501 for ethanol content and ASTM D6304 for water content. A distinct phase separation was noted in the sample container that was taken from the bottom of the tank. The very bottom layer in the sample container was clear with the layer just above being quite cloudy. When the samples were analyzed, an interesting distribution of water and ethanol were noted (See Table 6). Messrs. Jim Peeples and Paul Vind, both of O_2Diesel, Inc., indicated that this situation may occur when water, in excess of 1000 ppm, enters the fuel. To prevent phase separation, about 250 gallons from the bottom of the tank were removed and discarded. The concentration of OCTIMAX™ 4931 was then increased to 1.0 percent, and the concentration of ethanol remaining in the fuel was again measured. Additional anhydrous ethanol was added to the tank to bring the concentration back to about 7.7 percent in order to complete the durability testing. A sample of the fuel was taken and analyzed for ethanol and water. For emission measurements, a portion of the original 211b baseline fuel was blended with 1.0 percent OCTIMAX™ 4931 and 7.7 percent ethanol in a drum (EM-4904-F). Table 7 presents the measured fuel properties for the base fuel and the fuel used for emission measurements.

Table 6. Ethanol and Water Content from Main Fuel Tank After Phase Separation

Sample Position	Ethanol, wt. %	Water, ppm
Top	5.3	846
2 ft from Bottom	5.3	867
1 ft from Bottom	5.1	1119
Top Phase (Bottom)	0.7	619
Bottom Phase (Bottom)	49.97	499670

5. Unscheduled Maintenance

During initial engine operation (4.7 hours), an error code was noted and a loss in engine power was observed. The engine error code indicated that the engine was not receiving a signal from the vehicle speed sensor. Apparently, this engine was originally set up as a truck engine, and the electronic control module (ECM) required a signal for vehicle speed. This signal was disabled to resolve the problem, and durability operation was continued.

At about 29.1 hours of operation, a drop in power was once again observed. When the error codes were examined, the power loss was determined to originate in Cylinder 4. The error code indicated that the injector pulse response time was very short, and the injector was not functioning properly. Durability was continued to 29.8 hours while engine diagnostics were being performed. When the engine was stopped, the power had decreased by about 15 percent. At this point, the error codes indicated that Cylinders 4, 5, and 6 were not functioning properly due to short pulse response time, with Cylinder 4 having a total loss in power. No problems were noted for Cylinders 1 through 3. The injectors were removed and sent to M & D Distributors to be examined for a pop test and disassembled. According to Mr. Paul Vind, O_2Diesel, Inc., the injectors showed a good pop test. M & D Distributors was unable to flow test the injectors because they did not have the correct apparatus. The injectors were disassembled and no wear was observed, nor was any physical fault with the injectors observed. In addition, samples of the base fuel and O_2Diesel™ were analyzed for lubricity using ASTM D6078 and ASTM D6079. Table 8 presents the results of these measurements. These results indicated that the fuel lubricity of O_2Diesel™ was even better than the base fuel with a higher seize weight for the Ball On Cylinder Lubricity Evaluation (BOCLE) and a smaller scar with the High Frequency Reciprocating Rig (HFRR).

Table 7. Fuel Analysis

Fuel Property	211(b) Specification for Base Fuel	Analysis		
		Base Fuel (EM-4870-F)	Durability Fuel (EM-4873-F)	Emissions Fuel (EM-4904-F)
API Gravity	33±1	32.2	33.5	33.3
Sulfur, wt%	0.05±0.0025	0.0508	0.0425	0.0447
Cetane Number	45.2±2	43.5	40.8	45.4
Cetane Index	45.7±2	43.7	42.6	45.1
Aromatics, vol %	38.4±2.7	38.1	37.2	37.6
Olefins, vol %	1.5±0.4	1.7	1.8	2.2
Saturates, vol %	60.1±2.0	60.2	53.3	53.1
Distillation Parameters				
10%, °F	433±5	428	173	172
50%, °F	516±5	520	507	512
90%, °F	606±5	601	601	608
Additives				
Corrosion Inhibitor, ptb[a]	Required	4.5	–[b]	--
Demulsifier, ptb	Required	2	--	--
Anti-oxidant, ptb	Required	2	--	--
Metal Deactivator, ptb	Required	2	--	--

[a]ptb-pounds per thousand barrels
[b]Concentration not increased over the amount in the base fuel

Table 8. Lubricity Measurements

ASTM Method	Property	Base Fuel	O_2Diesel™
D6078	BOCLE, g	4150	6050
D6079	HFRR, mm	0.37	0.214

Each injector was reassembled and reinstalled in the engine with Injector 4, 5, and 6 being placed in positions 1, 2, and 3 to see if a similar loss in engine power was observed in the new positions. This installation showed the same loss in total engine power except that the error codes shifted with the injectors rather than the location. New injectors were ordered and installed. In a conference call between Jim Peeples, O_2Diesel, Inc., and with Dave Kortum from the EPA, it was determined that, under the regulations, a post-maintenance emissions test was not required if engine maintenance was conducted

during the 125-hour engine break-in. However, if the maintenance was required during the emissions testing part of the program, then a post-maintenance emissions test would be required. Engine durability was continued at 29.8 hours with the new injectors to complete a total of 125 hours of engine operation. At that point, the engine was placed in a transient-capable test cell for emissions testing.

III. Description of Analytical Methods

Regulated and unregulated emission measurements conducted for this program, as required by the Environmental Protection Agency (EPA), included the following items:

- Measurement of regulated emissions including total hydrocarbons (THC), carbon monoxide (CO), oxides of nitrogen (NO_x), and total particulate
- Speciation of vapor-phase and semi-volatile hydrocarbon compounds, alcohols, ethers, aldehydes, and ketones conducted for the first cold- and hot-start segment of the FTP
- Measurement of semi-volatile (vapor- and particulate-bound) PAH and NPAH. PAH compounds included: benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, chrysene, dibenzo[a,h]anthracene, and indeno[1,2,3-cd]pyrene; and NPAH compounds included: 7-nitrobenzo[a]anthracene, 6-nitrobenzo[a]pyrene, 6-nitrochrysene, 2-nitrofluorene, and 1-nitropyrene.

Regulated emissions (THC, CO, NO_x, and particulate) and carbon dioxide (CO_2) were analyzed according to Code of Federal Regulations (CFR) Title 40 specifications, and all applicable accuracy and calibration requirements were met. Analyses of unregulated emissions were conducted according to CRC, EPA, and SwRI analytical procedures. Applicable SwRI Standard Operating Procedures are listed in References 1 through 20. Table 9 presents the sampling requirements for each of the measured emissions.

A. Regulated Emissions

Regulated emissions were quantified in a manner consistent with EPA protocols for heavy-duty emissions testing as given in 40 CFR Part 86, Subpart D. Proportional exhaust gas samples were collected in Tedlar bags and analyzed for CO and CO_2 using non-dispersive infrared (NDIR) instruments, THC and NO_x were monitored continuously using a flame ionization detector and a chemiluminescent instrument, respectively. Wet absorption techniques were employed to collect alcohols, ethers, aldehydes and ketones. These wet absorption techniques are discussed in more detail below.

Two sizes of filters were used to collect particulate samples. These filters included the following:

- One set of 90-mm Pallflex (fluorocarbon-coated glass fiber) filters for determination of total particulate mass
- 20×20-inch Pallflex (fluorocarbon-coated glass fiber) filters for total dilute exhaust filtration of particulate; all filters were extracted individually for PAH and NPAH analyses.

Table 9. Sample Collection

Test Code	Test Day	Regulated THC, CO, NO_x, Part.	Speciation C_1 - C_{12}	Aldehydes/ Ketones	Alcohols and Ethers	PAH/NPAH	
						Vapor	Particulate
O_2Diesel™							
4904-C1	1	Cont., Bag, 90mm Filter	Bag	Bubbler	Bubbler	4 PUF Traps	1 20×20 Filter
4904-H1		Cont., Bag, 90mm Filter	Bag	Bubbler	Bubbler		1 20×20 Filter
4904-H12							
4904-H13							
4904-H14							
4904-H15							
4904-H16							
4904-C2	2	Cont., Bag, 90mm Filter	Bag	Bubbler	Bubbler	4 PUF Traps	1 20×20 Filter
4904-H21		Cont., Bag, 90mm Filter	Bag	Bubbler	Bubbler		1 20×20 Filter
4904-H22							
4904-H23							
4904-H24							
4904-H25							
4904-H26							
4904-C3	3	Cont., Bag, 90mm Filter	Bag	Bubbler	Bubbler	4 PUF Traps	1 20×20 Filter
4904-H31		Cont., Bag, 90mm Filter	Bag	Bubbler	Bubbler		1 20×20 Filter
4904-C32							
4904-H33							
4904-H34							
4904-H35							
4904-H36							
211b Baseline Fuel							
4870-C1	4	Cont., Bag, 90mm Filter	Bag	Bubbler	Bubbler	4 PUF Traps	1 20×20 Filter
4870-H11		Cont., Bag, 90mm Filter	Bag	Bubbler	Bubbler		1 20×20 Filter
4870-H12							
4870-H13							
4870-H14							
4870-H15							
4870-H16							
Blank 1						4 PUF Traps	1 20×20 Filter

Table 9 (Cont'd). Sample Collection

Test Code	Test Day	Regulated THC, CO, NO_x, Part.	Speciation C_1 - C_{12}	Aldehydes/ Ketones	Alcohols and Ethers	PAH/NPAH	
						Vapor	Particulate
4870-C2	5	Cont., Bag, 90mm Filter	Bag	Bubbler	Bubbler	4 PUF Traps	1 20×20 Filter
4870-H21		Cont., Bag, 90mm Filter	Bag	Bubbler	Bubbler		1 20×20 Filter
4870-H22							
4870-H23							
4870-H24							
4870-H25							
4870-H26							
4870-C3	6	Cont., Bag, 90mm Filter	Bag	Bubbler	Bubbler	4 PUF Traps	1 20×20 Filter
4870-H31		Cont., Bag, 90mm Filter	Bag	Bubbler	Bubbler		1 20×20 Filter
4870-H32							
4870-H33							
4870-H34							
4870-H35							
4870-H36							

All filters were conditioned and weighed in accordance with the appropriate sections of the CFR for heavy-duty engines.

B. Speciation of Volatile Hydrocarbon Compounds

Volatile hydrocarbon compounds were determined by hydrocarbon speciation. Analytical procedures for conducting the hydrocarbon speciation (C_1 to C_{12} hydrocarbons, aldehydes, and ketones) were similar to the CRC Auto/Oil Phase II methods. With these methods, exhaust emissions samples are analyzed for the presence of more than 200 different exhaust species. Four gas chromatography (GC) procedures and one High Performance Liquid Chromatograph (HPLC) procedure were used to identify and quantify specific compounds. One GC is used for the measurement of methane, a second for C_2-C_4 species, and a third for C_5-C_{12} species including two ethers (methyl tertiary butyl ether - MTBE and ethyl tertiary butyl ether - ETBE). A fourth GC was used to measure 1-methylcyclopentane, benzene, toluene, and 2,3,3-trimethylpentane, which co-elute and cannot be accurately quantified by other methods. In general, all emission "sample" bags were analyzed before the "background" bags, so that reactive exhaust compounds could be analyzed as quickly as possible. A brief description of these procedures is given below.

1. Methane Speciation

Methane levels were determined using proportional exhaust gas samples collected in Tedlar bags. A GC equipped with an FID was utilized for the analyses, and was used in accordance with SAE J1151 procedures. The GC system was equipped with a packed column to resolve methane from other hydrocarbons in the sample. Samples were introduced into a 5-mL sample loop via a diaphragm pump. For analysis, the valve was switched to the inject position, and the helium carrier gas swept the sample from the loop toward the detector through a 61 cm × 0.3 cm Porapak N column in series with a 122 cm × 0.3 cm molecular sieve 13X column. As soon as the methane peak passed into the molecular sieve column, the helium flow was reversed through the Porapak N column to vent. For quantification, sample peak areas were compared to those of external calibration standards.

2. C_2-C_4 Species

With the aid of a DB-WAX pre-column and a 10-port switching valve, the second GC procedure allows the separation and determination of exhaust concentrations of C_2-C_4 individual hydrocarbon species, including: ethane; ethylene; acetylene; propane; dimethylpropane; propyne; 1,3-butadiene; 2-methylpropane; 1-butyne; and cis-2-butene. Bag samples were analyzed with a GC system which utilizes a Hewlett-Packard Model 5890 Series II GC with an FID, two pneumatically operated and electrically controlled valves, and two analytical columns. The carrier gas was helium. One column is utilized to separate the C_2-C_4 hydrocarbons from the higher molecular weight hydrocarbons and the polar compounds. These higher molecular weight hydrocarbons (and water and alcohols) are retained on the pre-column while the C_2-C_4 hydrocarbons are passed through to the analytical column. While the C_2-C_4 hydrocarbons are separated on the analytical column, the pre-column is back-flushed with helium to prepare for the next run. The column flow was set by fine-tuning the column head pressure to give butane a retention time of 5.25 ± 0.05 minutes. The GC was calibrated daily using a CRC Auto/Oil 23-component calibration mixture. Detection limits for the procedure were on the order of 5 ppbC in dilute exhaust for all compounds.

3. C_5-C_{12} Species

The third GC procedure provides separation and exhaust concentrations for more than 100 C_5-C_{12} individual hydrocarbon compounds. Bag samples were analyzed using a gas chromatograph equipped with an FID. The GC system utilizes a Hewlett-Packard Model 5890 Series II GC with an FID, a pneumatically operated and electrically controlled valve, and a DB-1 fused silica open tubular column (FSOT). The carrier gas was helium. Gaseous samples are pumped from the bag through a sample loop and then introduced into a liquid nitrogen cooled column. The column oven was then programmed to a maximum temperature of 200°C. The analog signal from the FID was sent to a networked computer system via a buffered analog to digital converter. Column flow was set by fine-tuning the column head pressure to give propane a retention time of 5.40 ± 0.10 minutes using a temperature program. The GC was calibrated daily using a CRC Auto/Oil 23-component calibration mixture. Detection limits for the procedure are on the order of 10 ppbC in dilute exhaust for all compounds.

4. Benzene and Toluene

The fourth GC procedure uses a separate system configured similarly to the third GC method (but utilizing a DB-5 analytical column instead of a DB-1 FSOT column) to resolve individual concentrations of benzene and toluene according to the CRC Auto/Oil Phase II Protocols. Separation of benzene and toluene from co-eluting peaks was carried out by fine-tuning the column head pressure to give benzene a retention time of 22 to 23 minutes. The GC was calibrated daily using a CRC 7-component calibration mixture.

5. Aldehydes and Ketones

An HPLC procedure was utilized for the analysis of aldehydes and ketones. Samples were collected by bubbling dilute exhaust at a nominal flowrate of 4 L/min through chilled glass impingers containing an

acetonitrile solution of 2,4-DNPH and perchloric acid. For analysis, a portion of the acetonitrile solution was injected into a liquid chromatograph equipped with a UV detector. External standards of the aldehyde and ketone DNPH derivatives were used to quantify the results. The aldehydes and ketones measured were: formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, isobutyraldehyde/methylethylketone (not resolved from each other during normal operating conditions, and so split equally between the two compounds), benzaldehyde, valeraldehyde, o-tolualdehyde, m-tolualdehyde/p-tolualdehyde (not resolved from each other during normal operating conditions, and so reported together), and hexanaldehyde. Detection limits for this procedure are on the order of 0.005 ppm aldehyde or ketone in dilute exhaust.

C. Alcohols and Ethers

The measurement of alcohols and ethers in exhaust was accomplished by bubbling the exhaust through glass impingers containing deionized water. Two glass impingers in series, with each containing 25 mL of deionized water were used to collect exhaust samples for the analysis. The two glass impingers collect 99+ percent of the lower molecular weight alcohols which are soluble in water. Table 10 lists a number of alcohols and ethers that range in solubility from miscible to slightly soluble in water. The temperature of the collection impingers was maintained at 0-5°C with an ice water bath, and the flow rate through the impingers was maintained at 4 L/minute by the sample pump. A dry gas meter was used to determine the total flow through the impingers. The temperature of the gas stream was monitored by a thermocouple immediately prior to the dry gas meter. A drier was included in the system to prevent condensation in the pump, flowmeter, dry gas meter, etc. The flowmeter in the system allowed continuous monitoring of the sample to ensure proper flowrates during the sampling. The Teflon line connecting the CVS and the solenoid valve was heated to approximately 235°F in order to prevent water from condensing in the sample line.

The exhaust sample was collected continuously during the test cycle. Upon completion of each transient cycle, the impingers were removed, and the contents were transferred to a 30 mL polypropylene bottle and capped. For analysis, a 1.0 µL portion of the aqueous solution was injected into a Hewlett-Packard 5890 GC equipped with a FID and a 7673 auto sampler. The analytical column was a 0.32 mm X 30 m DB-WAX column with a 1.0 µm film thickness. The carrier gas was helium and was set to give optimum separation (20 mL/minute). To quantify the results, the sample peak areas were compared to the peak areas of standard solutions. External standards containing methanol and ethanol in deionized water were used to quantify the results. In addition, 1-propanol, 2-propanol, and tertiary butanol were analyzed for retention time identification should they have appeared. No other compounds were detected in the water samples and, if present, were below the detection limits for the procedure. Detection limits for the lower molecular weight alcohols with this procedure are on the order of 0.06 ppm in dilute exhaust.

Table 10. Selected C_1 to C_6 Alcohols and Ethers That Have Some Solubility in Water

Compound	Empirical Formula
Alcohols	
Methanol	CH_4O
Ethanol	C_2H_6O
2-Propyn-1-ol	C_3H_4O
Allyl alcohol	C_3H_6O
Isopropanol	C_3H_8O
n-Propanol	C_3H_8O
Crotyl alcohol	C_4H_8O
n-Butanol	$C_4H_{10}O$
sec-Butanol	$C_4H_{10}O$
tert-Butanol	$C_4H_{10}O$
Isobutanol	$C_4H_{10}O$
Furfuryl alcohol	$C_5H_6O_2$
2-Methyl-3-butyn-2-ol	C_5H_8O
Cyclopentanol	$C_5H_{10}O$
Tetrahydrofurfuryl alcohol	$C_5H_{10}O_2$
Isopentanol	$C_5H_{12}O$
2-Methyl-1-butanol	$C_5H_{12}O$
3-Methyl-2-butanol	$C_5H_{12}O$
Neopentanol	$C_5H_{12}O$
1-Pentanol	$C_5H_{12}O$
2-Pentanol	$C_5H_{12}O$
3-Pentanol	$C_5H_{12}O$
tert-Pentanol	$C_5H_{12}O$
Phenol	C_6H_6O
3-Methyl-1-pentyn-3-ol	$C_6H_{10}O$

Table 10 (Cont.) Selected C_1 to C_6 Alcohols and Ethers That Have Some Solubility in Water

Compound	Empirical Formula
Cyclohexanol	$C_6H_{12}O$
4-Hydroxy-4-methyl-2-pentanone	$C_6H_{12}O_2$
2,2-Dimethyl-1,3-dioxolane-4-methanol	$C_6H_{12}O_3$
2,5-Tetrahydrofurandimethanol	$C_6H_{12}O_3$
1-Hexanol	$C_6H_{14}O$
Ethers	
Methyl ether	C_2H_6O
Methyl ethyl ether	C_3H_8O
Vinyl ether	C_4H_6O
Cyclopropyl methyl ether	C_4H_8O
Ethyl ether	$C_4H_{10}O$
Methyl propyl ether	$C_4H_{10}O$
Isopropyl ether	$C_6H_{14}O$
Propyl ether	$C_6H_{14}O$

D. PAH and NPAH

In addition to the regulated and C_1 to C_{12} hydrocarbon exhaust emissions, semi-volatile (vapor- and particulate-phase) PAH and NPAH compounds were also determined for each fuel. Seven PAH compounds were quantified: benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, chrysene, dibenzo[a,h]anthracene, and indeno[1,2,3-cd]pyrene; and five NPAH compounds: 7-nitrobenzo[a]anthracene, 6-nitrobenzo[a]pyrene, 6-nitrochrysene, 2-nitrofluorene, and 1-nitropyrene. A 400 in^2 fluorocarbon-coated glass fiber filter (20×20-inch Pallflex filter) was used to collect the particulate-phase PAH and NPAH, and a PUF/XAD/PUF sandwich adsorbent trap was used to collect the vapor-phase PAH and NPAH. The PUF/XAD/PUF traps contained a layered sampling media consisting of a 1.25 inch deep layer of polyurethane foam (PUF), a 0.5 inch deep layer of XAD-2 resin, and a second 1.25 inch deep layer of PUF. The XAD-2 resin was incorporated to improve the trapping efficiency for NPAH compounds, which were potentially present in much lower levels than PAH compounds.

Both XAD-2 and PUF sample media were cleaned prior to use as described below. The XAD-2 was cleaned by siphoning four times with water using a Soxhlet followed by the residual water being vacuumed off, Soxhlet extracted with methanol for 24 hours, Soxhlet extracted with toluene for 48 hours, and finally Soxhlet extracted with methylene chloride for 48 hours. The residual methylene chloride was removed as much as possible and then totally removed by purging with heated nitrogen. For PUF cleaning, each foam disk was Soxhlet extracted for 24 hours with acetone, for 48 hours with hexane/ether, and finally for 24 hours with acetone.

Vapor- and particulate-phase PAH and NPAH samples were obtained using a separate secondary dilution tunnel, which was operated in parallel with a smaller secondary dilution tunnel used to obtain the 90-mm filter samples for particulate mass determinations. The PAH and NPAH tunnel was considerably larger than the one with 90-mm filter to allow for the use of 20×20-inch Pallflex sampling media for the particulate-phase PAH and NPAH compounds and the use of the four specially designed PUF/XAD/PUF traps for the vapor-phase PAH and NPAH compounds. Filter samples were generated during the cold-start and the six hot-start tests, although only samples from the cold-start and the first hot-start were analyzed individually. PUF/XAD/PUF trap samples were collected during the entire test sequence (one cold- and six hot-starts combined).

Vapor-phase PAH and NPAH samples presented a particular problem for heavy-duty sampling because conventional sampling techniques would not allow for sufficient sample to be gathered to meet EPA detection requirements. Commercially available sampling media and hardware were of insufficient size to allow for the collection of sample volumes needed to meet these detection limits. Sampling media size was also limited by the ability to extract and concentrate samples obtained. Therefore, an approach was devised involving both custom built sampling hardware and a modified sampling plan. The PUF/XAD/PUF traps were sized to allow a media diameter of 4 inches, rather than the conventional 2.5 inches. This larger diameter allowed a much higher flowrate to be used, while maintaining the face velocity within recommended levels for the smaller, conventional sampling media.

The combination of using four larger sample media cartridges and the collection of samples over multiple test runs allowed for the accumulation of a sample volume similar to that passing through a 20×20-inch filter during a single test (roughly 3000 standard cubic feet of dilute exhaust). This volume of dilute exhaust sample was sufficient for the analysis to meet the required detection threshold of 1 ng/hp-hr. A sample set for a given test day consisted of a cold-start filter sample, a hot-start filter sample, and a set of four PUF/XAD/PUF traps for the vapor-phase PAH and NPAH. Background PAH and NPAH sample sets were obtained by operating the sampling systems with sampling media loaded, but without the engine operating, for about two hours.

Following testing, sample sets were delivered to the laboratory for analysis. In cases where immediate extraction was not possible, samples were stored at 4°C. Filters and PUF/XAD/PUF traps were extracted separately. Prior to extraction of the filters, each filter was spiked with a surrogate solution containing 100 ng each of six deuterated PAH: benzo[a]anthracene-d12, chrysene-d12, benzo[b]fluoranthene-d12, benzo[k]fluoranthene-d12, benzo[a]pyrene, and dibenzo[a,h]anthracene-d14 in order to verify recovery during the extraction process. The samples were then Soxhlet extracted for 8 hours with ethanol/toluene (70/30 v/v). Prior to extraction, each PUF/XAD/PUF trap was spiked with a surrogate solution containing 200 ng each of six deuterated PAH: benzo[a]anthracene-d12, chrysene-d12, benzo[b]fluoranthene-d12, benzo[k]fluoranthene-d12, benzo[a]pyrene, and dibenzo[a,h]anthracene-d14 in order to verify recovery during the extraction process. The trap samples were then extracted for at least 8 hours with methylene chloride. At this point, both filter and trap samples were treated similarly. One half of each filter or trap extract was cleaned using dilute sulfuric acid and an activated silica gel column. The extracts were then reduced to 500 µL in toluene; and just prior to analysis, 100 µL of the extract was spiked with 30 ng of benzo[e]pyrene-d12 for PAH and 10 ng each of 2-nitrofluorene-d9, 1-nitropyrene-d9, 6-nitrochrysene-d11, and 6-nitrobenzo[a]pyrene-d11 for NPAH.

Samples for both the vapor- and the particulate-phase PAH and NPAHs were analyzed by GC/MS (gas chromatograph/mass spectroscopy) using an Agilent 5973N MSD with a 30 m X 0.32 mm i.d. DB-5 column and a 0.25 µm film thickness. For each analysis, a 2 µL aliquot of the sample extract was injected into the instrument. A calibration curve consisting of at least five points was obtained prior to sample analysis to ensure linearity, and a mid-point continuing calibration was performed each day after the

initial five point calibration. Analysis of NPAH compounds was performed using the negative ion chemical ionization (NI/CI) mode and for PAH compounds using the positive ion electron impact (PI/EI) mode. Two or three characteristic ions for each PAH and NPAH were monitored. Separate GC/MS analyses were necessary to acquire both the PAH and NPAH data. Each target compound met the criterion of a 30 percent relative response (RRF) factor and 30 percent deviation in relation to the mean RRF obtained in the initial and continuing calibration.

IV. Quality Control and Quality Assurance

In order to demonstrate SwRI's constant goal to provide quality emissions data in our project efforts, the Department of Emissions Research maintains accreditation to ISO 9002 and ISO/IEC Guide 25 standards. Standard operating procedures and routine instrument calibration and calibration records are included in these standards. Based on the successful completion of laboratory audits, the SwRI Department of Emissions Research is able to maintain registration under ISO 9002, "Model for Quality Assurance in Production and Installation," and accreditation by ISO/IEC Guide 25, General Requirements for the Competence of Calibration and Testing Laboratories." Presented below is the SwRI Department of Emissions Research Quality Policy Statement:

> **SwRI Department of Emissions Research Quality Policy Statement**
> *"A key dimension of the services we provide is high quality that is self-evident to our clients and the technical community. Every individual contribution to our research, development, evaluation, and certification projects is intended to further our clients' success and to fulfill the mission of the Institute. Our commitment is to continuously improve our ability to meet changing needs in our discipline and deliver all we have agreed to do, or more, while sustaining a climate of consideration and adherence to ethical standards in our workplace. Implementation of our quality program will be relied on for maintaining our market position, our personal growth and satisfaction, and the long-term expansion of our activity."*

Throughout this project, SwRI implemented our QA/QC plan in a manner consistent with the program objectives, including spot-checking of records, accuracy/precision charts, notebooks, calibration tags, and other quality control elements including chain of custody of samples. Listed below are a few of the regular procedures that ensure the quality standards are maintained.

- **Senior Scientist/Technician Review** - A system for formal data review is in place in the SwRI DER. All technicians review their work prior to submitting it to the data computations laboratory for calculation of final concentrations. The Project Leader reviews the results before a test is accepted.
- **Interlaboratory Comparisons/Round Robins** - SwRI has participated in numerous Round Robin exercises to correlate the results of our laboratory with other accepted facilities. Those Round Robin studies which are directly related to this project include: CRC Round Robin Analysis of Alcohol and Carbonyl Synthetic Exhaust Samples (results published in SAE Paper No. 941944); and CRC Round Robin Hydrocarbon Speciation Analysis of Synthetic Exhaust Gas (results not yet published).
- **Lab Audits** - Internal audits are conducted by the DER Quality Coordinator as specified in DER Quality Policy and Program 12, "Internal Audits."
- **Project Records** - Documents directly associated with a technical project, such as: correspondence, proposals, contracts, work orders, cost sheets, invoices, interim and final reports, and follow-up contacts are maintained. All records come under Standard Operating Procedure (SOP), document SOP-14-001, "Storage and Maintenance of DER Records" (Reference 21).
- **Calibration Records** - Data sheets, chart recordings, computer printouts, log books, calibration and maintenance logs, and spreadsheets associated with the calibration of measurement equipment are maintained. Also includes calibration results from external suppliers.
- **Engine and Vehicle Testing Records** - Data sheets, chart recordings, log books, start/stop logs,

and computer printouts associated with evaluation and testing of engines and vehicles are retained.

- **Chemistry Calibration and Analysis Records** - Data sheets, log books, and spreadsheets associated with calibration and analyses performed in the chemistry areas are retained.
- **Data Reduction and Test Result Records** - Computed results, tables, and spread sheets generated using information obtained from emissions testing and chemical analysis are maintained. Records developed in the areas specified in SOP 14-001 are retained for a period of ten years.

V. Test Results

Emission testing was performed on the exhaust from a 2002 Detroit Diesel heavy-duty diesel engine. Tests with O_2Diesel™ were performed after a total of 125 hours of engine operation with the fuel. Three cold- and eighteen hot-start tests were utilized for the emissions characterizations. The fuel was changed to the 211b baseline fuel, durability operation was performed for about five hours, and an additional set of emissions tests were conducted.

A. Regulated Emissions

After the 125 hours of engine operation, the average composite regulated emissions were lower than or equal to the corresponding 2002 emission standards with both fuels, except for particulate. When CO, NO_x, and particulate emissions with the O_2Diesel™ were compared to the 211b baseline fuel, the O_2Diesel™ was found to produce about 6 percent lower CO and NO_x emissions and about 7 percent lower particulate emissions. The THC emissions were increased by about 40 percent when compared to the 211b baseline fuel. Table 11 summarizes the regulated emissions with each fuel. Appendix A contains the individual and composite emission test results.

B. Speciation of Volatile Hydrocarbon Compounds

Speciation of the volatile hydrocarbon compounds with carbon numbers from C_1 to C_{12} plus aldehydes, ketones, and two ethers (methyl tertiary butyl ether - MTBE and ethyl tertiary butyl ether - ETBE) was performed for each cold- and hot-segment of the EPA transient cycle. More than 200 compounds were checked for their presence in the dilute exhaust. Data for the individual compounds, corrected for background dilution air contributions, are included in Appendix B. A composite result for the triplicate tests is also included in Appendix B.

In general, all compounds found in the exhaust with the O_2Diesel™ were also found in the exhaust with the 211b baseline diesel fuel. One exception was with an unidentified C_8 compound that was detected at very low concentrations in only two of the three hot-start tests with the O_2Diesel™. No additional compounds were found in the exhaust from the O_2Diesel™ as compared to the 211b baseline fuel at or above the detection limits for the analytical procedures.

Table 11. Summary of Regulated Emissions

Test	Emissions Results, g/bhp-hr			
	THC	CO	NO_X	Particulate
2002 Standard	1.3	16	4.0	0.10
O_2Diesel™				
4904 C1	0.32	1.9	3.9	0.17
4904 H11	0.26	1.4	3.4	0.13
Composite	0.27	1.5	3.4	0.13
4904 C2	0.29	1.8	4.0	0.17
4904 H21	0.27	1.5	3.5	0.13
Composite	0.27	1.5	3.6	0.13
4904 C3	0.37	1.9	4.0	0.15
4904 H31	0.30	1.5	3.6	0.13
Composite	0.31	1.6	3.6	0.13
Average of Three Composites	0.28	1.5	3.6	0.13
211b Baseline Fuel				
4870 C1	0.23	1.9	4.0	0.15
4870 H11	0.15	1.5	3.7	0.13
Composite	0.16	1.6	3.8	0.13
4870 C2	0.34	2.0	4.1	0.17
4870 H21	0.22	1.5	3.8	0.13
Composite	0.24	1.6	3.8	0.14
4870 C3	0.36	2.1	4.0	0.17
4870 H31	0.19	1.6	3.7	0.14
Composite	0.21	1.7	3.7	0.15
Average of Three Composites	0.20	1.6	3.8	0.14

While no additional compounds which could be identified were found with the O_2Diesel™, some differences did occur in the individual concentrations. Six compounds were detected in the 211b baseline diesel fuel that were **not** detected with the O_2Diesel™. These compounds included:

- butane
- trans-2-butene
- 3-methyl-1-butene
- hexane
- 2,4-dimethylhexane
- trans-4-octene.

In addition, five aldehydes (formaldehyde, acetaldehyde, acrolein, acetone, and benzaldehyde) were detected at 27, 54, 72, 54, and 85 percent higher concentration, respectively, in the O_2Diesel™ than in the exhaust of the 211b baseline diesel fuel. Some compounds were also found in either one or more of the cold- or one or more of the hot-starts during the triplicate test sequence. In other cases, some compounds were detected at less than two times the detection limit for the compound when calculated as a composite value or as an average. These compounds are labeled as "trace" in the Appendix tables.

C. Alcohols and Ethers

The only alcohols or ethers up to C_6 that were detected with either of the two fuels were methanol, ethanol, and isopropanol. Methanol was detected in the exhaust from the O_2Diesel™ at about the same concentration as levels found in the exhaust from the 211b baseline fuel. Isopropanol was detected in trace amounts with both fuels. Ethanol was detected at about an order of magnitude greater in the exhaust from the O_2Diesel™ when compared to the levels found in the exhaust from the 211b baseline fuel. These results were expected because ethanol is a component of the fuel formulation for the O_2Diesel™. While the other water soluble alcohols and ethers were below the detection limit, one cannot conclude that these compounds were present or not present; but if present, they were below the limits of detection. Table 12 lists the results for these analyses.

D. PAH and NPAH

Vapor- and particulate-phase semi-volatile PAH and NPAH compounds were also determined for each fuel. The seven PAH compounds included: benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, chrysene, dibenzo[a,h]anthracene, and indeno[1,2,3-cd]pyrene; and the five NPAH compounds included: 7-nitrobenzo[a]anthracene, 6-nitrobenzo[a]pyrene, 6-nitrochrysene, 2-nitrofluorene, and 1-nitropyrene. The analytical procedure used to measure these compounds was able to detect less than 1 ppm (equivalent to 1 ng/mg organic extract) for this analysis. Values were reported in terms of ng/bhp-hr. Samples were collected from the vapor- and particulate-phases of exhaust. Table 13 presents the vapor-phase PAH and NPAH results, and Table 14 presents the particulate-phase results.

Table 12. Vapor Phase Alcohol Results

Compound	Cold	Hot	Composite	Cold	Hot	Composite	Cold	Hot	Composite	Average Composite, mg/hp-hr
	mg/hp-hr	mg/hp-hr	mg/hp-hr	mg/hp-hr	mg/hp-hr	mg/hp-hr	mg/hp-hr	mg/hp-hr	mg/hp-hr	
O_2Diesel™										
Methanol	2.6	2.4	2.4	4.7	4.1	4.2	6.0	7.1	6.9	4.5
Ethanol	29	28	28	27	29	29	35	35	35	31
1-Propanol	ND[a]	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Propanol	Trace[b]	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace	Trace
t-Butanol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
211b Baseline Fuel										
Methanol	6.3	4.2	4.5	3.4	1.8	2.0	4.6	4.4	4.4	3.7
Ethanol	5.2	2.8	3.1	13.1	2.4	3.9	1.9	1.4	1.5	2.8
1-Propanol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2-Propanol	Trace	ND	Trace	Trace	ND	Trace	ND	Trace	ND	Trace
t-Butanol	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

[a]ND - None detected.
[b]Trace - Value not quantifiable.
Note: No other alcohols were detected at the limits of detection for this procedure.

Table 13. Vapor Phase Semi-Volatile PAH and NPAH Results

Compound	O_2Diesel™, ng/hp-hr				211b Baseline Fuel, ng/hp-hr			
	Composite C1	Composite C2	Composite C3	Average	Composite C1	Composite C2	Composite C3	Average
2-Nitrofluorene[a]	ND[b]	ND	ND	ND	ND	ND	ND	ND
1-Nitropyrene[c]	ND	ND	ND	ND	ND	ND	ND	ND
7-Nitrobenz(a)anthracene	5.6	6.8	6.4	6.3	5.5	5.8	5.9	5.7
6-Nitrochrysene[c]	ND	ND	ND	ND	ND	ND	ND	ND
6-Nitrobenz(a)pyrene[c]	ND	ND	ND	ND	ND	ND	ND	ND
Benzo(a)anthracene	10	16	13	13	5.1	5	3.5	4.5
Chrysene	17	16	19	17	2.7	4.1	2.3	3.0
Benzo(b)fluoranthene	2.4	4.5	4.1	3.7	1.2	1.2	1.2	1.2
Benzo(k)fluoranthene	3.2	5.2	4.4	4.3	3.5	3.9	4.3	3.9
Benzo(a)pyrene	3.9	4.7	4.8	4.5	1.9	2.6	2.6	2.4
Indeno[1,2,3-cd]pyrene	2.3	3.5	3.6	3.1	1.5	1.1	1.1	1.2
Dibenz(a,h)anthracene[c]	ND	ND	ND	ND	ND	ND	ND	ND

[a]Detection limit in ng/hp-hr calculated using the minimum value that could be quantified by the analytical procedure; if present, the PAH/NPAH was at a concentration less than 0.4 ng/hp-hr.
[b]ND - None detected; calculated detection indicated.
[c]Detection limit in ng/hp-hr calculated using the minimum value that could be quantified by the analytical procedure; if present, the PAH/NPAH was at a concentration less than 0.8 ng/hp-hr.

Table 14. Particulate Phase Semi-Volatile PAH and NPAH Results

Compound	C1, ng/hp-hr			C2, ng/hp-hr			C3, ng/hp-hr			Average Composite, ng/hp-hr
	Cold	Hot	Composite	Cold	Hot	Composite	Cold	Hot	Composite	
O_2Diesel™										
2-Nitrofluorene	19	9.9	11	14	10	11	9.8	20	19	14
1-Nitropyrene	168	94	105	150	77	87	105	68	73	88
7-Nitrobenz(a)anthracene	9.5	9.9	9.8	9.6	5	5.7	20	20	20	12
6-Nitrochrysene[a]	trace[b]	trace	trace	ND[c]	trace	trace	trace	ND	trace	trace
6-Nitrobenz(a)pyrene[a]	ND	ND	ND	ND	ND	ND	ND	trace	trace	trace
Benzo(a)anthracene	6200	4900	5100	4400	3500	3600	4400	4000	3900	4200
Chrysene	12300	10300	10600	8800	7800	7900	8200	6000	6600	8400
Benzo(b)fluoranthene	3400	2300	2400	2800	2900	2700	3200	2800	2700	2600
Benzo(k)fluoranthene	3500	3400	3400	2600	2300	2300	2900	2200	2400	2700
Benzo(a)pyrene	4700	4000	4100	4000	3900	3900	3900	3600	3500	3800
Indeno[1,2,3-cd]pyrene	2300	2100	2200	1900	2100	2000	2100	1800	1900	2000
Dibenz(a,h)anthracene	208	136	146	118	124	123	141	95	106	125

[a]Detection limit in ng/hp-hr calculated using the minimum value that could be quantified by the analytical procedure; if present, the PAH/NPAH was at a concentration less than 5.0 ng/hp-hr.
[b]Trace - Value not quantifiable
[c]ND - None detected; calculated detection indicated.

Table 14 (Cont'd). Particulate-Phase Semi-Volatile PAH and NPAH Results

Compound	C1, ng/hp-hr			C2, ng/hp-hr			C3, ng/hp-hr			Average Composite, ng/hp-hr
	Cold	Hot	Composite	Cold	Hot	Composite	Cold	Hot	Composite	
211b Baseline Fuel										
2-Nitrofluorene	48	9.8	15	9.4	29	26	38	15	18	20
1-Nitropyrene	107	118	117	197	100	114	210	75	94	108
7-Nitrobenz(a)anthracene	43	34	35	9.4	33	30	9.5	9.8	9.7	25
6-Nitrochrysene[a]	trace[b]	ND[c]	trace	ND	trace	trace	trace	trace	trace	trace
6-Nitrobenz(a)pyrene[a]	ND	ND	ND	trace	ND	trace	ND	ND	ND	trace
Benzo(a)anthracene	3700	3500	3500	4100	4500	4500	4000	3800	3800	3900
Chrysene	7300	5300	5600	8000	6600	6800	7100	6300	6400	6300
Benzo(b)fluoranthene	2200	1900	1900	2600	2700	2700	2700	2300	2300	2300
Benzo(k)fluoranthene	2300	1800	1900	2500	1900	2000	2400	2000	2000	2000
Benzo(a)pyrene	3300	2700	2800	3400	2900	3000	3000	3000	3000	2900
Indeno[1,2,3-cd]pyrene	1300	1200	1200	1800	1400	1500	1400	1500	1500	1400
Dibenz(a,h)anthracene	94	57	62	115	84	88	112	68	73	74

[a]Detection limit in ng/hp-hr calculated using the minimum value that could be quantified by the analytical procedure; if present, the PAH/NPAH was at a concentration less than 5.0 ng/hp-hr.
[b]Trace - Value not quantifiable.
[c]ND - None detected; calculated detection indicated.

No vapor-phase PAH or NPAH compounds were detected with the O_2Diesel™ that were not found with the 211b baseline fuel. The vapor-phase PAHs were between 2 and 6 times higher with the O_2Diesel™, except for benzo(k)fluoranthene and for dibenz(a,h) anthracene which was not detected in any of the vapor-phase samples at the limits of detection. For the vapor-phase NPAH compounds, only 7-nitrobenz(a)anthracene was detected with either fuel.

For the particulate-phase, all PAH and NPAH compounds were present at quantifiable levels except 6-nitrochrysene and 6-nitrobenz(a)pyrene which were only detected at trace quantities. All NPAH compounds were about two orders of magnitude lower in concentration than the PAH compounds for both fuels.

As a means of comparing the PAH and NPAH results, the vapor- and particulate-phases were combined to obtain a total value for both fuels. These total values were obtained by averaging the results for the three individual tests with each sample and adding the two values together. Table 15 summarizes the results in terms of the combined phases for each compound. As can be seen from the table, the particulate-phase compounds were detected at much higher rates that the vapor-phase results.

Table 15. Combined Vapor- and Particulate-Phase PAH and NPAH Results

Compound	O_2Diesel™, µg/hp-hr			211b Baseline Fuel, µg/hp-hr		
	Vapor	Particulate	Total	Vapor	Particulate	Total
2-Nitrofluorene	ND[a]	0.014	0.014	ND	0.02	0.020
1-Nitropyrene	ND	0.088	0.088	ND	0.108	0.108
7-Nitrobenz(a)anthracene	0.006	0.012	0.018	0.006	0.025	0.031
6-Nitrochrysene	ND	trace[b]	trace	ND	trace	trace
6-Nitrobenz(a)pyrene	ND	trace	trace	ND	trace	trace
Benzo(a)anthracene	0.01	4.20	4.21	0.01	3.90	3.91
Chrysene	0.02	8.40	8.42	0.00	6.30	6.30
Benzo(b)fluoranthene	0.00	2.60	2.60	0.00	2.30	2.30
Benzo(k)fluoranthene	0.00	2.70	2.70	0.00	2.00	2.00
Benzo(a)pyrene	0.01	3.80	3.81	0.00	2.90	2.90
Indeno[1,2,3-cd]pyrene	0.00	2.00	2.00	0.00	1.40	1.40
Dibenz(a,h)anthracene	ND	0.13	0.13	ND	0.07	0.07

[a]ND - None detected at detection limit.
[b]Trace - Value not quantifiable.

VI. Summary

Testing was performed on a heavy-duty engine to provide O_2Diesel, Inc. with data in support of the EPA requirements for registration of a designated F/FA as stipulated by section 211 (b) and 211 (e) of the CAA. A 2002 Detroit Diesel engine was tested according to procedures established in 40 CFR 79.57 and 40 CFR 86 Subpart D. Emissions characterization was performed on the engine after 125 hours of operation with O_2Diesel™. The fuel was changed to the 211b baseline fuel, and the engine was operated for about five hours. At this point, tests were once again conducted to characterize the emissions.

In general, the composite regulated emissions were lower than or equal to the 2002 emission standards except for particulate. When the CO, NO_x, and particulate emissions from O_2Diesel™ were compared to the emissions from the 211b baseline fuel, the O_2Diesel™ produced about 6 percent less CO and NO_x emissions, and about 7 percent less particulate emissions (See Table 16). The THC emissions were increased by about 40 percent when compared to the 211b baseline fuel. Speciation of the C_1 to C_{12} hydrocarbons including C_1 to C_6 alcohols and ethers, aldehydes, and ketones was performed during each cold- and hot-segment of the EPA transient cycle. In general, compounds measured in the exhaust with the O_2Diesel™ were also present in the exhaust with the 211b baseline fuel, except for an unidentified C_8 compound which was detected in only two hot-start tests with the O_2Diesel™. Ethanol, formaldehyde, acetaldehyde, acrolein, acetone, and benzaldehyde were found at higher concentrations than in the exhaust of the 211b baseline fuel. No additional compounds, which could be attributed to the use of O_2Diesel™, were found in the exhaust at the detection limits for the analytical procedures.

In addition, vapor- and particulate-phase PAH and NPAH compounds were measured in the exhaust with both fuels. Some vapor-phase PAH compounds with the O_2Diesel™ were detected at about two to six times the levels detected in the exhaust from the 211b baseline fuel. However, the vapor-phase PAH compounds for both fuels were about two orders of magnitude lower than the particulate-phase compounds for both fuels. No PAH or NPAH compounds were detected with the O_2Diesel™ that were not found in the 211b baseline fuel. While selected individual C_1 to C_{12} hydrocarbons and selected C_1 to C_6 alcohols and ethers were determined to be below the detection limit, one cannot necessarily conclude that these compounds were present or not present; however if present, the compounds were below the limits of detection.

Table 16. Summary of Composite Regulated Emissions

Test	Emissions Results, g/bhp-hr			
	THC	CO	NO_X	Particulate
2002 Standard	1.3	16	4.0	0.10
O_2Diesel™				
Composite C1-H11	0.27	1.5	3.4	0.13
Composite C2-H21	0.27	1.5	3.6	0.13
Composite C3-H31	0.31	1.6	3.6	0.13
Average of Three Composites	0.28	1.5	3.6	0.13
211b Baseline Fuel				
Composite C1-H11	0.16	1.6	3.8	0.13
Composite C2-H21	0.24	1.6	3.8	0.14
Composite C3-H31	0.21	1.7	3.7	0.15
Average of Three Composites	0.20	1.6	3.8	0.14

References

1. DER SwRI SOP 06-001 “Traceability to Standards.”
2. DER SwRI SOP 06-002 “NO_x Converter Efficiency Determination.”
3. DER SwRI SOP 06-003 “Linearity Verification of Gas Dividers.”
4. DER SwRI SOP 06-010 “Barometric Pressure Verification.”
5. DER SwRI SOP 06-011 “Propane Recovery Check.”
6. DER SwRI SOP 06-013 “Temperature Calibration and Verification.”
7. DER SwRI SOP 06-016 “Wet CO_2 Interference Check for CO Analyzers.”
8. DER SwRI SOP 06-020 “Pressure Calibration and Verification.”
9. DER SwRI SOP 06-022 “CVS Blower Calibration.”
10. DER SwRI SOP 06-023 “Calibration of Analyzers Using Digital Readout.”
11. DER SwRI SOP 07-023 “Operation of Bag Cart.”
12. DER SwRI SOP 07C-002 “Methane Quantitative Analysis.”
13. DER SwRI SOP 07C-006 “Analysis of Aldehydes and Ketones in Exhaust by Liquid Chromatography.”
14. DER SwRI SOP 07C-010 “Impinger Sampling of Exhaust Emissions.”
15. DER SwRI SOP 07C-011 “Preparation of Impingers Used in Collection of Unregulated Emissions.”
16. DER SwRI SOP 07C-013 “Hydrocarbon Speciation.”
17. DER SwRI SOP 08-003 “Data Transfers and Calculations - HD, LD, and NR.”
18. DER SwRI SOP 08-006 “Calculation of Aldehyde and Ketone Results.”
19. DER SwRI SOP 08-007 “Calculation of Methane Results.”
20. DER SwRI SOP-14-001, "Storage and Maintenance of DER Records.”

Appendix A

Heavy-Duty Emission Test Results

Page	Test No.
O_2Diesel™	
A-1	4904 C1
A-2	4904 H11
A-3	4904 C1/4904 H11 Composite
A-4	4904 C2
A-5	4904 H21
A-6	4904 C2/4904 H21 Composite
A-7	4904 C3
A-8	4904 H31
A-9	4904 C3/4904 H31 Composite
211b Baseline Fuel	
A-10	4870 C1
A-11	4870 H11
A-12	4870 C1/4870 H11 Composite
A-13	4870 C2
A-14	4870 H21
A-15	4870 C2/4870 H21 Composite
A-16	4870 C3
A-17	4870 H31
A-18	4870 C3/4870 H31 Composite

Appendix B

HYDROCARBON SPECIATION DATA

Appendix C

Test Substance Information

OCTIMAX™ 4931
containing
proprietary surfactants
and
2-ethylhexyl nitrate

MANUFACTURER
O_2Diesel, Inc.
200 Executive Drive
Newark, Delaware 19702

CONTACT PERSON
Jim Peeples
Phone: (703) 256-4497

The O_2Diesel, Inc. additive technology is an ethanol-based diesel fuel containing up to 7.7 percent ethanol as the primary additive and OCTIMAX™ 4931 as the blending additive. OCTIMAX™ 4931, a proprietary additive technology of O_2Diesel, Inc., is produced by Octel Starreon LLC and is based on the chemistry of proprietary surfactants. These proprietary surfactants are blended at a concentration greater than 75 percent with 2-ethylhexyl nitrate (CAS No. 27247-96-7) at a concentration of less than 25 percent to produce the blending additive OCTIMAX™ 4931. OCTIMAX™ 4931 is blended with the diesel and alcohol at concentrations up to 1.0 percent. When OCTIMAX™ 4931 is blended with diesel fuel and 7.7 percent ethanol, the product is referred to as O_2Diesel™. This 211b test protocol was employed to test for a 7.7 percent ethanol and diesel fuel blend utilizing 1.0 percent concentration of the OCTIMAX™ 4931 additive technology. Material Safety Data Sheets (MSDS) for OCTIMAX™ 4931 and O_2Diesel™ are included in Appendix C.

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	February 2004	Subcontractor Report

4. TITLE AND SUBTITLE
Fuel and Fuel Additive Registration Testing of Ethanol-Diesel Blend for O_2Diesel, Inc.

5. FUNDING NUMBERS
ZCL-3-32068-01
BBA3.5110

6. AUTHOR(S)
E. Robert Fanick, Southwest Research Institute

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
AAE Technologies Inc
200 Executive Drive
Newark DE 19702

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401-3393

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
NREL/SR-540-35334

11. SUPPLEMENTARY NOTES
NREL Technical Monitor: R. McCormick

12a. DISTRIBUTION/AVAILABILITY STATEMENT
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*
O_2 Diesel Inc. (formerly AAE Technologies Inc.) tested a heavy duty engine with O_2Diesel (diesel fuel with 7.7% ethanol and additives) for regulated emissions and speciation of vapor-phase and semi-volatile hydrocarbon compounds. This testing was performed in support of EPA requirements for registering designated fuels and fuel additives as stipulated by sections 211(b) and 211(e) of the Clean Air Act.

14. SUBJECT TERMS
O_2Diesel; ethanol-diesel

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL